I. A STUDY OF THE CYCLIZATION TENDENCY OF AN *ORTHO* METHYL CHALCONE

II. NEW METHODS FOR MAKING *PERI* DERIVATIVES IN THE NAPHTHALENE AND ACENAPHTHENE SERIES

BY

GEORGE EDWARD MUNN

B. S., Westminster College, 1945

AN ABSTRACT OF A THESIS

SUBMITTED IN PARTIAL FULFILLMENT OF THE REQUIREMENTS
FOR THE DEGREE OF DOCTOR OF PHILOSOPHY IN CHEMISTRY
IN THE GRADUATE COLLEGE OF THE
UNIVERSITY OF ILLINOIS, 1948

URBANA, ILLINOIS

1948

I. A STUDY OF THE CYCLIZATION TENDENCY OF AN *ORTHO* METHYL CHALCONE

II. NEW METHODS FOR MAKING *PERI* DERIVATIVES IN THE NAPHTHALENE AND ACENAPHTHENE SERIES

BY

GEORGE EDWARD MUNN

B. S., Westminster College, 1945

AN ABSTRACT OF A THESIS

SUBMITTED IN PARTIAL FULFILLMENT OF THE REQUIREMENTS
FOR THE DEGREE OF DOCTOR OF PHILOSOPHY IN CHEMISTRY
IN THE GRADUATE COLLEGE OF THE
UNIVERSITY OF ILLINOIS, 1948

URBANA, ILLINOIS

1948

ACKNOWLEDGMENT

The author wishes to express his sincere appreciation to Professor Reynold C. Fuson for suggesting this study and for his advice during the course of this investigation.

PART ONE

A STUDY OF THE CYCLIZATION TENDENCY OF AN *ORTHO* METHYL CHALCONE

Introduction

It has been shown that in the Michael condensation, the equilibrium favors the formation of a strainless ring in preference to an intermolecular reaction.[1,2,3] In this study, it was proposed to prepare a chalcone containing an *ortho* methyl group which is activated by two nitro groups, and to study the tendency of such a compound to undergo an intramolecular Michael reaction.

Discussion of Results

The following method was used for the preparation of 2′-methyl-3′,5′-dinitrochalcone. 3,5-Dinitro-*o*-toluyl chloride was allowed to condense with either the sodium or ethoxymagnesium salt of malonic ester, and the resulting product was hydrolyzed to yield 2-methyl-3,5-dinitroacetophenone. In the presence of hydrogen chloride, this compound condensed with benzaldehyde to form 2′-methyl-3′,5′-dinitrochalcone.

When this chalcone was treated with bromine in acetic acid, a monobromo derivative which is thought to be 2′-methyl-3′,5′-dinitro-α-bromochalcone was obtained.

Although ring closure would not occur, the 2′-methyl-3′-5′-dinitrochalcone was found to undergo a Michael condensation with malonic ester, thus showing that this chalcone has very little tendency for ring closure.

When the malonic ester adduct was hydrolyzed, 2-phenyl-3-(2-methyl-3,5-dinitrobenzoyl)-butyric acid was obtained.

PART TWO

NEW METHODS FOR MAKING *PERI* DERIVATIVES IN THE NAPHTHALENE AND ACENAPHTHENE SERIES

Introduction

In the course of a study concerning the formation of large *peri* rings, it was necessary to investigate new methods for the preparation of *peri* derivatives of compounds containing the naphthalene or acenaphthene nucleus.

Most *peri* derivatives of naphthalene are synthesized from the oxidation products of compounds which contain a *peri* ring. 1,8-Naphthaldehydic acid has been prepared from acenaphthequinone by the action of potassium hydroxide.[4] The oxidation of *peri*-naphthindan-1,3-dione with potassium permanganate produces naphthalonic acid.[5] This compound has been reduced with phosphorus and hydriodic acid to form 1,8-naphthalide and 8-methyl-1-naphthoic acid.[6]

In the acenaphthene series, *peri* derivatives may be made by direct substitution. Most of these compounds which have been studied have identical substituents in both of the *peri* positions such as 5,6-diacetylacenaphthene,[7,8] thus limiting their use as intermediates for the synthesis of compounds containing different groups in the *peri* positions.

This investigation was undertaken to study new methods for the preparation of *peri* derivatives of naphthalene and acenaphthene which are suitable intermediates for further syntheses.

Discussion of Results

The synthesis of 1,8-naphthaldehydic acid[4] has been studied and improved. This compound was found to undergo a crossed Cannizzaro reaction to form 1,8-naphthalide. The

reduction of 1,8-naphthalide with Raney's nickel-aluminum alloy and sodium hydroxide produced tetrahydro-8-methyl-1-naphthoic acid, a compound which was also made by the catalytic hydrogenation of naphthalic anhydride. A Clemmensen reduction of 1,8-naphthaldehydic acid yielded 8-methyl-1-naphthoic acid which was found to melt at 153° instead of 130-131° as has been reported in the literature.[6]

The oxidation of 5-acetylacenaphthene produced 5-acenaphtheneglyoxal which rearranged when treated with potassium hydroxide to form 5-acenaphtheneglycolic acid. Reduction of this compound with hydriodic acid produced 5-acenaphtheneacetic acid. Acetylation of methyl 5-acenaphtheneacetate yielded methyl 6-acetyl-5-acenaphtheneacetate and a diacetyl derivative of unknown structure.

It was found that 5-acenaphthenacetyl chloride would not cyclize under the influence of stannic chloride or aluminum chloride to form aceacenaphthenone.

5-Acenaphthonitrile was prepared from 5-bromoacenaphthene by means of the Rosenmund-von Braun synthesis.

BIBLIOGRAPHY

1. Kohler and Dewey, *J. Am. Chem. Soc.*, **46,** 1267 (1924).
2. Helmkamp, Taughe, and Plati, *ibid.*, **62,** 3215 (1940).
3. Kohler and Helmkamp, *ibid.*, **46,** 1018 (1924).
4. Graebe and Gfeller, *Ber.*, **25,** 653 (1892).
5. Errera and Cuffaro, *Gazz. chim. ital.*, **41 II,** 807 (1911).
6. Errera and Ajon, *ibid.*, **44 II,** 95 (1914).
7. Fleisher and Wolff, *Ber.*, **53,** 925 (1914).
8. Dziewonski and Spirer, *Bull. intern. acad. polonaise,* **1931** *A,* 232.

VITA

The author was born in Lawrence County, Pennsylvania, on November 29, 1924. He attended the public schools of Mahoning Township and was graduated from Union Township High School in June, 1941. In June, 1942, he entered Sterling College at Sterling, Kansas, where he was a student until August, 1943. That fall he entered Westminster College at New Wilmington, Pennsylvania, where he received the degree of Bachelor of Science in Chemistry in June, 1945.

In the fall of 1945, he enrolled in the Graduate College of the University of Illinois, where he held a teaching assistantship until June, 1947, and a University Fellowship from that time until June, 1948.

Digitized by the Internet Archive
in 2026

https://archive.org/details/IA41549807_0011